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- (3) Proprietor: PENNWALT CORPORATION Pennwalt Building Three Parkway Philadelphia Pennsylvania 19102 (US)
- (1) Inventor: Brooks, Wayne E.
  2104 Lazy Oaks
  Bryan Texas 77801 (US)
  Inventor: Walker, Morris P.
  Route 8, Box 498
  Benton Kentucky 42025 (US)
  Inventor: Hodges, Jimmie Ray
  1408 Crestmont Drive
  Downingtown Pennsylvania 19335 (US)
- Representative: Kraus, Walter, Dr. et al, Patentanwälte Dres. Kraus & Weisert Irmgardstrasse 15
  D-8000 München 71 (DE)

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Continuous process for the direct conversion of potassium chloride to potassium chlorate by electrolysis

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This invention relates to a continuous-loop process for the direct production by electrolysis of potassium chlorate from potassium chloride, comprising the steps of:

(a) electrolyzing an aqueous solution of potassium chloride in an electrolytic cell having a metal cathode and a coated metal anode, said coating comprising a precious metal, a precious metal alloy, a precious metal oxide or a platinate,

(b) removing from said cell an effluent solution containing potassium chlorate formed by said electrolysis of potassium chloride;

(c) cooling said effluent until crystals of the chlorate form;

(d) removing said chlorate crystals from said effluent;

(e) enriching said effluent by adding a controlled amount of potassium chloride thereto; and

(f) returning and adding the enriched effluent to said electrolytic cell for further electrolysis, at a volume rate equal to the rate at which the unenriched effluent is removed from the cell in step (b).

A process of this kind is described in US—A—4 046 653. This process for the direct production of KClO<sub>3</sub> from KCl requires high temperature (90 to 110°C) operation and a special cell design to achieve very high electrolyte flow and uses insulation of the reactor rather than cooling.

Historically, commercial quantities of potassium chlorate have been produced by the double decomposition of sodium chlorate and potassium chloride;

The sodium chlorate used in this process has ordinarily been produced directly by the electrolysis of an aqueous sodium chloride solution in an electrolytic cell. To each batch of sodium chlorate produced potassium chloride is added stoichiometrically; the resultina KCIO /NaCI solution is cooled; and the KCIO, crystals that form are separated from the solution. The industry practice has been to boil down the remaining solution, or mother liquor, to adjust the water concentration to the level employed in the electrolytic cell and to return the concentrated liquor to the cell for further electrolysis with the NaCl added by the above reaction to produce more sodium chlorate according to the reaction

Since the separation of KClO<sub>3</sub> is not 100% efficient, potassium ions will inevitably be present in the concentrated liquor returned to the cell, necessitating the operation of the cell at high temperatures to prevent the crystallization of the potassium. These high temperatures and the potassium ions present cause very rapid wear results in high equipment costs, while labor costs are elevated by the fact this process is carried out in a batch, rather than on a continuous, basis.

US-A-3,883,406 is directed to a process for recovering electrolytically produced alkali metal chlorates obtained by the direct electrolysis of sodium chloride to sodium chlorate in diaphragmless cells equipped with dimensionally stable anodes of a valve metal, such as titanium, coated with a noble metal and/or oxide thereof. The discussion of the prior art in this patent explains that NaCl is less soluble than NaClO<sub>3</sub> at the temperatures conventionally used, so that during the concentration and evaporative cooling steps of the prior art, NaCl crystals separate from the cell liquor first and are removed by filtration or centrifugation. This NaCl may then be redissolved and returned to the cell. US-A-3,883,406 itself discloses processes wherein solutions are achieved having chlorate concentrations in excess of 700 grams NaCIO, per liter and chloride concentrations as low as 40 grams NaCl per liter. At the high chlorate/chloride concentrations obtained. evaporative cooling causes the chlorate to crystallize first if sufficient vacuum is applied. The particular advantages of the process disclosed in US-A-3,883,406 are achieved by electrolyzing the NaCl solution to produce a ratio of NaClO<sub>3</sub>:NaCl of at least 5:1 and preferably at least 7:1.

When the direct electrolysis of alkali metal chlorides to alkali metal chlorates in aqueous solution is carried out, chlorine is produced at the anode while alkali metal hydroxide forms at the cathode. The chlorine and hydroxyl ions are thus free to react chemically to form alkali metal hypochlorite, as is shown by the following equation illustrating the process with potassium:

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The hypochlorite rapidly converts to form chlorate;

## 3 KCIO → 2 KCI + KCIO<sub>3</sub>

The reversible nature of the formation of alkali metal hypochlorite accounts for significant process inefficiencies where oxygen is liberated into the cell liquor when the hypochlorite decomposes instead of disproportionating into the chloride and the chlorate. Prior to the advent of metal anodes, the direct production of potassium chlorate was uneconomical because the low solubility of KClO<sub>3</sub> in water at the temperature previously employed (e.g. 4—5% in H<sub>2</sub>O at 30°C) limited the recovery of KClO<sub>3</sub> when compared with the yields available in the conventional double decomposition process.

US-A-4,046,653 discloses a process for producing sodium or potassium chlorate by the direct electrolysis of the corresponding chloride at temperatures of 90-110°C. The working example that discloses the electrolysis of potassium chloride starts with a solution containing 300 g per liter of solution as a starting electrolyte, achieving concentrations of 90 g/l potassium chloride and 210 g/l potassium chlorate at steady state operating conditions. While this patent discloses the discharge of an equal volume of electrolyte from the cell as the KCI brine is fed in, we have determined that it is not possible to operate a closed loop process in accordance with this patent using only a saturated brine without adding additional solld KCI directly to the cell electrolyte and that the results stated are not significantly different from those expected from the electrolysis of sodium chloride.

The object of the present invention is to overcome the disadvantages of the prior art processes and particularly to avoid the high temperature operation and the special cell design of the process described in US—A—4,046,653.

According to the present invention this object is achieved by the fact that the effluent in an intermediate step is passed through a heat exchanger through which is passed water at a temperature which is above the temperature at which KCIO<sub>3</sub> crystallized from solutions of the concentration selected for the process.

Thus, the present invention is based upon the findings that heated cooling water is needed to prevent premature precipitation of potassium chlorate which would plug the apparatus. The inventive process provides for closed loop production and high current efficiency.

The inventive continuous closed-loop process for directly producing potassium chlorate by electrolysis of an aqueous potassium chloride solution, provides the first practical metal anode process for producing potassium chlorate by electrolysis and provides surprising advantages in efficiency by comparison with the conventional double

decomposition process for producing potassium chlorate from sodium chlorde.

This invention provides a continuous closedloop process for the direct production by electrolysis of potassium chlorate from potassium chloride, wherein an aqueous solution of potassium chloride is electrolyzed in a suitable electrolytic cell having a metal cathode and a metal anode coated with a precious metal or a precious metal oxide. The base of the metal anode may be a metal selected from titanium, zirconium, tantalum and hafnium, with titanium being preferred. The coating may be a precious metal, for example, platinum, etc.; an alloy, for example platinum-iridium alloy, etc.; an oxide, for example ruthenium oxide, titanium oxide, etc., including mixtures thereof; or a platinate, for example lithium platinate, calcium platinate etc. After the solution has been subjected to electrolysis and at least part of the potassium chloride in the solution has been converted to potassium chlorate, the solution is removed as an effluent from the cell and is cooled until crystals of the chlorate form. This cooling may be adiabatic, e.g. under a vacuum, or it may be carried out by refrigeration. After the crystals have formed, they are removed from the effluent by conventional means. The effluent that remains is enriched by adding a controlled amount of potassium chloride to the effluent either as solid potassium chloride or as a concentrated potassium chloride brine. This enriched effluent is then returned to the electrolytic cell as part of the aqueous solution for further electrolysis, at a volume rate equal to the rate at which the unenriched effluent is removed from the cell for cooling crystalliza-

In particular, this invention involves a process wherein the effluent removed from the electrolytic cell contains 8-20% by weight KCI and 8-20% by weight KCIO3, in the ratio of 0.5-2.5 parts by weight KCI to each part by weight KClO<sub>3</sub>. In particular, the effluent may contain 10% KCIO<sub>3</sub> by weight and less than 15% KCI by weight. The invention further comprehends electrolytic cell effluents which contain 10-14% KCIO3 and 10-16% by weight KCL. As will be discussed further below, the operation parameters of the process in accordance with this invention are described in Figs. 2 and 3 of the drawings. The process according to this invention may be particularly carried out within the area HIJK as set forth in Fig. 2.

In addition to the above characteristics and attributes, the process in accordance with our invention may also include a step, interposed in the process at the point after which the effluent is removed from the electrolytic cell and before the effluent is subjected to cooling crystallization, wherein any elemental chlorine present in the effluent is stripped therefrom. In carrying out the process in accordance with this invention, which is exothermic in nature, we have

found that the temperature of the electrolytic cell can be controlled when the cell is equipped with coils or, preferably, when the cell liquor is passed through a heat exchanger through which is passed water at a temperature which is above the temperature at which the KCIO3 will crystallize from aqueous solutions when it is present in the concentrations selected for use in the process. This may be accomplished in an intermediate step, either before or after crystallizing the KClO<sub>3</sub> from the effluent. After operation of the cell over a period of time, the concentrations of KCI and KCIO3 in the electrolyte will reach an equilibrium. In the resaturation or enriching step that is part of the invention herein, sufficient solid KCI, or KCI brine, is added to the effluent to restore the KCI concentration in the enriched effluent that is returned to the cell to the level of KCL concentration in the equilibrium solution electrolyzed in the cell.

One of the main features of this invention is the provision for the first time of a practical continuous closed-loop process for the direct conversion of potassium chloride to potassium chlorate, without the attendant inefficiencies of the prior double decomposition process.

Another important feature of this invention is the provision of a process for producing potassium chlorate that can be practiced in the same apparatus used to convert sodium chloride to sodium chlorate electrolytically, while providing unexpected increases in current efficiency and power consumption.

Yet another feature of the invention is that it provides a process for producing potassium chlorate that may be practiced within a wide range of operating conditions without detriment to the efficiency of the process.

Fig. 1 is a flow diagram depicting the process of this invention.

Fig. 2 is an equilibrium phase diagram showing graphically the parameters of the broad scope of this invention.

Fig. 3 is an equilibrium phase diagram depicting the more preferred parameters of operation of the process according to this invention.

In this invention potassium chloride Is converted by direct electrolysis into potassium chlorate in electrolytic cells using titanium anodes, for example. Process cells as disclosed US-A-3,824,173 either US-A-4,075,077 may be used. The cells are operated individually or in groups employing series or parallel flow, so that the final cell product contains 8-20% KCIO<sub>3</sub> and 8-20% KCI. These solutions preferably have a ratio of chloride to chlorate of at least 0.5:1 and not more than 2.5:1. Flg. 1 shows the steps of the process by reference to the apparatus components and general process conditions we employ.

When the cell product, or effluent, is removed from the cell or cells, it may optionally

be passed through a stripper to remove dissolved elemental chlorine from the effluent before it is cooled. The stripped effluent liquor then passes to a cooling crystallizer, which may be operated either under a vacuum or with refrigeration. Preferably, the effluent is cooled under a high vacuum (0,95 bar) to a temperature of about 38°C (100°F) at which point KCIO<sub>2</sub> crystals form as a slurry at the bottom of the crystallizer. The KCIO, product is rendered from the slurry by a conventional cyclone and a centrifuge. The mother liquor effluent, now a dilute KCI solution with some residual KCIO, in it, passed through a resaturator, where solid KCI (or KCI brine) is added to restore the concentration of KCI in the liquor to its pre-electrolysis concentration. This enriched liquor is then returned to the electrolytic cell, completing the closed-loop process. Of course, water may also be added to the liquor in the resaturator to control cell concentrations. In carrying out this process persons skilled in this art will adjust the electrolyte pH, use suitable buffering agents, e.g., sodium dichromate, and otherwise optimize process conditions, in light of the disclosures of US-A-3,824,172 4,075,077 and conventional practices in this

The equilibrium phase diagrams Figs. 2 and 3 illustrate the parameters of operation of this process. In Fig. 2, area ABC represents the theoretical range covered by our process. Outside of area ABC it is not possible to perform the steps of electrolysis (line AB) crystallization (line BC) and resaturation with solid KCI or KCI brine (line CA). Realistically the process is most practicable within the area DEFG, while smaller area HIJK represents the desired range of operation for the continuous closed-loop process of this invention.

Fig. 3 depicts the operation within the area HIJK of Fig. 2, with the theoretical and practical limits of a particular process set-up added for emphasis. The area RbFaMR represents the theoretical limits of operation for the particular process design depicted, while area RdFcMR represents the practical limits of that same design. Points R, F and M delimit the process described in the Example below. Line A (connecting points R and F) represents the electrolytic conversion of KCl to KClO3; line B (connecting points F and M) represents the vacuum flash crystallization of KCLO, (at a temperature of about 37.8°C (100°F)), as indicated above); and line C (connecting points M and R) represents the resaturation of the effluent liquor with solid KCI, thus closing the material balance. Where crystallization is performed refrigeration rather than evaporative cooling under a vacuum, the crystallization line B on Fig. 3 will more closely approximate dM than line FM depicted. This, and other, modifications of the process are apparent to persons skilled in this art from an examination of Figs. 2 and 3.

The following example is a representative illustration of the process according to this invention as demonstrated in Fig. 3:

Example

pllot cell disclosed in (as US-A-3,824,172) of 5000 amperes capability was operated for 22 days to produce a liquor concentration of 150 g/l KClO<sub>3</sub> and 175 g/I KCI (13% KCIO<sub>3</sub> and 15.3% KCI respectively). The material was passed through a crystallizer tank operated at 37.8°C (100°F). The recycle liquor was returned to a saturator

tank where solid KCI was added to achieve the material balance. Solid KClO<sub>3</sub> was removed from the crystallizer tank, washed and analyzed. The cell liquor was maintained at 75°C by a heat exchanger on the circulating liquor. Hot water was used as the cooling media to prevent chlorate precipitation in the exchanger and the cell. The power consumption during this period averaged 3800 KWH (DC) per ton of KCIO<sub>3</sub> produced.

The particular, and surprising, advantages of the process according to our invention are illustrated by the following Table I:

# TABLE I

COMPARISON OF ELECTROLYSIS KCIO3 VERSUS NaCIO3

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= 6.5  $Na_{2}Cr_{2}O_{7} = 5.0 g/I$ 

Current Density <sub>2</sub> Amps/dm <sup>2</sup> (Amps/in <sup>2</sup> )	Temperature -	Power Usage DC.KWH/Ton		% Oxygen in Cell Gás		Cell Voltage	
		ксюз	NaC IO3	ксюз	NaCIO <sub>3</sub>	ксюз	NaCIO <sub>3</sub>
23.2 (1.5)	75.0 (167)	3,642	4,532	1,022	2.98	3.082	3,378
31,0 (2.0)	75.0 (167)	3,781	4,925	1.418	2.98	3.191	3.797
38,7 (2.5)	75.0 (167)	3,920	5,318	1.022	2.98	3.300	4.080

% Overall Current Efficiency KCIO<sub>3</sub> = 100.50

NaCIO<sub>3</sub>= 88.03

Ordinarily, whether a process is closed-loop or continuous is not of great importance, where the batch process is easily and cheaply carried out. However, when the findings of Table I are considered, it is apparent that the direct production of KClO<sub>3</sub> from KCl is unexpectedly more efficient than the production of NaClO<sub>3</sub> (and thus KCIO<sub>3</sub> by the double decomposition method) from NaCl under analogous process conditions. Our process may be carried out with same equipment disclosed US-A-3,883,406, but with results that provide efficiencies, based on electric power usage, of KCIO, production hitherto unavailable. Table I shows that under the same conditions of temperature and current density, the electrolysis of KCI to KCIO3 in accordance with our process is 12% more efficient, consumes 25% less power per ton of product and produces significantly less oxygen in the cell gas, as compared with the electrolysis of NaCl to

We have learned, subsequent to our making of this invention, that the efficiency of our

process is further enhanced by ensuring that the apparatus in which the process is carried out is constructed so that all portions of the system which come into contact with the effluent are substantially devoid of nickel and other transition elements, in particular copper, manganese, zinc and cobalt. It has been determined that the oxygen content of the cell gas, which negatively correlates with the efficiency of conversion of chloride to chlorate (the oxygen being liberated by the undesired decomposition of the hypochlorite intermediate), is significantly reduced from usual levels when the nickel and other transition metals loadings in the cell liquor are kept below 1 ppm.

Another refinement is the control of the water temperature, in the exchanger at a temperature which is above the temperature in which KCIO, will crystallize from aqueous solution when present in a particular concentration chosen for operation of the process. The electrolytic conversion of potassium chloride to potassium chlorate is known to be exothermic, but in the past, workers in this art have

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preferred to rely upon the rapid movement of the electrolyte itself through the cell to provide cooling. We have found that the process yields may be increased by permitting additional residence time in the cell, if the liquor is cooled, not with cold water, but with water that has a temperature which is selected to be below the equilibrium temperature of the cell, which is ordinarily about 75°C (167°F), but above the temperature at which KCIO<sub>3</sub> will crystallize from the solution along the walls of the cell. This method also has the advantage of reducing power consumption for cooling over either refrigerative cooling or providing cooling by rapid transport of electrolyte through the cell.

#### Claims

- 1. A continuous closed-loop process for the direct production by electrolysis of potassium chlorate from potassium chloride, comprising the steps of:
- (a) electrolyzing an aqueous solution of potassium chloride in an electrolytic cell having a metal cathode and a coated metal anode, said coating comprising a precious metal, a precious metal alloy, a precious metal oxide or a platinate,
- (b) removing from said cell an effluent solution containing potassium chlorate formed by said electrolysis of potassium chloride;
- (c) cooling said effluent until crystals of the chlorate form;
- (d) removing said chlorate crystals from said effluent;
- (e) enriching said effluent by adding a controlled amount of potassium chloride thereto; and
- (f) returning and adding the enriched effluent to said electrolytic cell for further electrolysis, at a volume rate equal to the rate at which the unenriched effluent is removed from the cell in step (b), characterized by the fact that the effluent in an intermediate step is passed through a heat exchanger through which is passed water at a temperature which is above the temperature at which KClO<sub>3</sub> crystallized from solutions of the concentration selected for the process.
- 2. The process of claim 1, wherein the effluent contains 8—20% by weight KCl and 8—20% by weight KClO<sub>3</sub>, in the ratio of 0.5—2.5 parts by weight KCl to each part by weight KClO<sub>3</sub>, and wherein the process is carried out within the area DEFG set forth in Fig. 2.
- 3. The process of claim 1, wherein the effluent contains 8—20% by weight KCl and 8—20% by weight KClo<sub>3</sub>, in the ratio of 0.5—2.5 parts by weight KCl to each part by weight KCLO<sub>3</sub>, and wherein the process is carried out within the area HIJK set forth in Fig. 2.
- 4. The process of claim 3, wherein the effluent contains 10% KClO<sub>3</sub> by weight and less

than 15% KCI by weight.

5. The process of claim 3, wherein the effluent contains 10—14% by weight KClO<sub>3</sub> and 10—16% by weight KCl.

6. The process of claim 3, 4 or 5, further including stripping any elemental chlorine present in said effluent obtained from step (b) before carrying out step (c).

7. The process of claim 3, 4 or 5, wherein the effluent is subjected to in step (b) to evaporate cooling.

8. The process of claim 3, 4 or 5, wherein enriching step (d) comprises adding sufficient solid KCI to the effluent to restore the KCI concentration in the enriched effluent returned to the cell to the level of KCI concentration in the aqueous solution of step (a).

9. The process of claim 3, 4, or 5, wherein the anode comprises a base of a metal selected from titanium, zirconium, tantalum and hafnium, coated with a material selected from the group consisting of platinum, platinum-iridium alloys and ruthenium oxide.

## Revendications

 Procédé continu en circuit fermé pour la production directe, par électrolyse, de chlorate de potassium à partir de chlorure de potassium, comprenant les étapes qui consistent:

(a) à électrolyser une solution aqueuse de chlorure de potassium dans une cellule électrolytique ayant une cathode en métal et une anode métallique revêtue, ledit revêtement comprenant un métal précieux, un alliage de métal précieux, un oxyde de métal précieux ou un platinate,

(b) à décharger de ladite cellule comme effluent une solution contenant du chlorate de potassium formé par ladite électrolyse du chlorure de potassium,

(c) à refroidir ledit effluent jusqu'à ce que des cristaux de chlorate se forment,

(d) à séparer lesdits cristaux de chlorate dudit effluent,

(e) à enrichir l'effluent en y ajoutant une quantité réglée de chlorure de potassium; et

(f) à recycler et introduire l'effluent enrichi dans ladite cellule électrolytique en vue d'une électrolyse ultérieure, à un débit en volume égal au débit auquel l'effluent non enrichi est déchargé de la cellule dans l'étape (b), caractérisé par le fait que dans une étape intermédiaire, ou fait passer l'effluent à travers un échangeur de chaleur dans lequel passe de l'eau à une température qui est au-dessus de la température à laquelle KCIO<sub>3</sub> cristallise dans des solutions de la concentration choisie pour le procédé.

2. Procédé suivant la revendication 1, dans lequel l'effluent contient 8 à 20% en poids de KCI et 8 à 20% en poids de KCIO<sub>3</sub>, dans le rapport de 0,5—2,5 parties en poids de KCI pour chaque partie en poids de KCIO<sub>3</sub>, et le procédé est mis en oeuvre dans les limites de

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l'aire DEFG représentée sur la figure 2.

3. Procédé suivant la revendication 1, dans lequel l'effluent contient 8 à 20% en poids de KCI et 8 à 20% en poids de KCIO3, dans le rapport de 0,5-2,5 parties en poids de KCI pour chaque partie en poids de KCIO3, et le procédé est mis en oeuvre dans les limites de l'aire HIJK représentée sur la figure 2.

4. Procédé suivant la revendication 3, dans lequel l'effluent contient 10% en poids de KCIO3

et moins de 15% en poids de KCl.

5. Procédé suivant la revendication 3, dans lequel l'effluent contient 10 à 14% en poids de KCIO<sub>3</sub> et 10 à 16% en poids de KCI.

6. Procédé suivant la revendication 3, 4 ou 5, impliquant en outre l'élimination de tout chlore élémentaire présent dans ledit effluent obtenu dans l'étape (b) avant la conduite de l'étape (c).

7. Procédé suivant la revendication 3, 4 ou 5, dans lequel l'effluent est soumis dans l'étape (b)

à un refroidissement par évaporation.

8. Procédé sulvant la revendication 3, 4 ou 5, dans lequel l'étape d'enrichissement (d) consiste à ajouter suffisamment de KCI solide à l'effluent pour rétablir la concentration en KCI de l'effluent enrichi recyclé dans la cellule au niveau de concentration en KCI de la solution aqueuse de l'étape)a).

9. Procédé suivant la revendication 3, 4 ou 5, dans lequel l'anode comprend un support d'un métal choisi entre le titane, zirconium, tantal et hafnium revêtu d'une matière choisie dans le groupe comprenant le platine, des alliages platine-iridium et l'oxyde de ruthénium.

### Patentansprüche

- 1. Kontinuierliches Verfahren mit gesch-Jossenem Kreislauf zur direkten Herstellung von Kaliumchlorat durch Elektrolyse aus Kaliumchlorid mit den Stufen
- (a) Elektrolyse einer wäßrigen Lösung von Kaliumchlorid in einer elektrolytischen Zelle mit einer Metallkathode und einer beschichteten Metallanode, wobei der Überzug ein Edelmetall, eine Edelmetallegierung, ein Edelmetalloxid oder ein Platinat umfaßt,
- (b) Entfernung einer Abstromlösung, die Kaliumchlorat, gebildet durch Elektrolyse von Kaliumchlorid, enthält, aus der Zelle,
- (c) Abkühlung des Abstroms bis zur Bildung von Kristallen von Chlorat,
- (d) Entfernung der Chloratkristalle aus dem
- (e) Anreicherung des Abstroms durch Zugabe einer kontrollierten Menge von Kaliumchlorid und

Zurückführung und Zugabe angereicherten Abstroms zu der elektrolytischen Zelle zur weiteren Elektrolyse mit einer Volumenrate, die der Rate gleich ist, mit der der nicht-angereicherte Abstrom von der Zelle in Stufe (b) entfernt wird, dadurch gekennzeichnet, daß man den Abstrom in einer Zwischenstufe durch einen Wärmeaustauscher leitet, durch den Wasser mit einer Temperatur geleitet wird, welche oberhalb der Temperatur liegt, bei der KCIO<sub>3</sub> aus Lösungen mit einer Konzentration, die für das Verfahren ausgewählt ist, auskristallisiert.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß der Abstrom 8 bis 20 Gew.-% KCI und 8 bis 20 Gew.-% KCIO, im Verhältnis von 0,5 bis 2,5 Gewichtsteilen KCI zu jedem Gewichtsteil KCIO<sub>3</sub> enthält, wobei das Verfahren innerhalb des Bereichs DEFG der

Figur 2 durchgeführt wird.

3. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß der Abstrom 8 bis 20 Gew.-% KCl und 8 bis 20 Gew.-% KClO3 im Verhältnis von 0,5 bis 2,5 Gewichtsteilen KČI zu jedem Gewichtsteil KCIO3 enthält, wobei das Verfahren innerhalb des Bereichs HIJK der Figur 2 durchgeführt wird.

4. Verfahren nach Anspruch 3, dadurch gekennzeichnet, daß der Abstrom 10 Gew.-% KCIO<sub>3</sub> und weniger als 15 Gew.-% KCl enthält.

5. Verfahren nach Anspruch 3, dadurch gekennzeichnet, daß der Abstrom 10 bis 14 Gew.-% KCIO3 und 10 bis 16 Gew.-% KCl enthält.

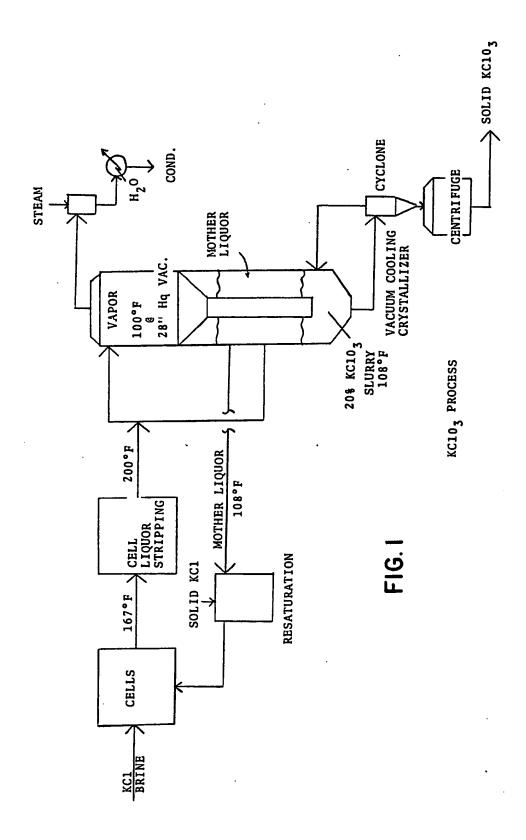
6. Verfahren nach Anspruch 3, 4 oder 5, dadurch gekennzeichnet, daß man weiterhin irgendwelches elementares Chlor, welches in dem Abstrom der Stufe (b) vorhanden ist, vor der Durchführung der Stufe (c) abstreift.

7. Verfahren nach den Ansprüchen 3, 4 oder 5, dadurch gekennzeichnet, daß man den Abstrom in der Stufe (b) einem Verdampfungskühlen unterwirft.

8. Verfahren nach den Ansprüchen 3, 4 oder 5, dadurch gekennzeichnet, daß man in der Anreicherungsstufe (d) genügend festes KCI zu dem Abstrom zusetzt, daß die KCI-Konzentration in dem angereicherten Abstrom, der In die Zelle zurückgeleitet wird, auf den Wert der KCI-Konzentration in der wäßrigen Lösung der Stufe (a) wiederhergestellt wird.

9. Verfahren nach den Ansprüchen 3, 4 oder 5, dadurch gekennzeichnet, daß die Anode eine Grundlage aus einem Metall, ausgewählt aus Titan, Zirkon, Tantai und Hafnium, welche mit einem Material, ausgewählt aus der Gruppe Platin-Iridium-Legierungen Rutheniumoxid, beschichtet ist, umfaßt.

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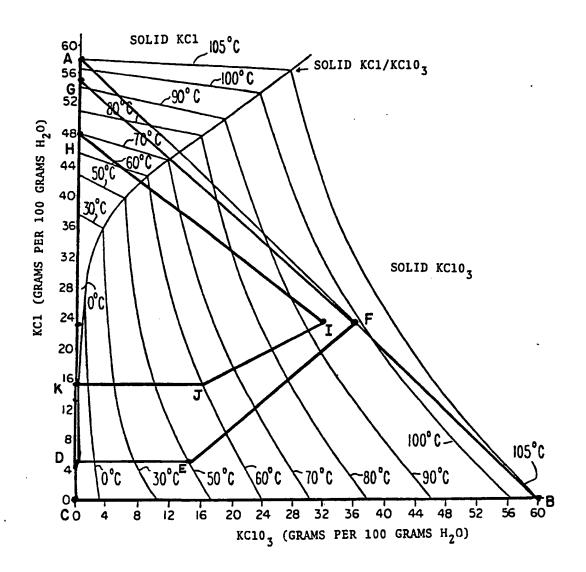
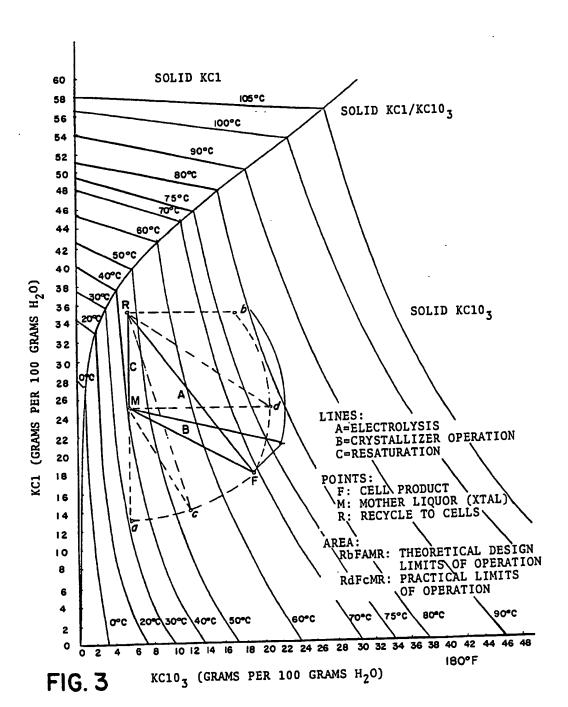


FIG. 2



3